Viscoelastic behavior of dental restorative composites during setting
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EXPERIMENTAL CONSIDERATIONS

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Abstract

This chapter describes the results of the process of optimizing an automated universal testing machine by which reliable stress-strain data can be obtained on the mechanical behavior of dental restorative materials during setting. The contents will be of interest to those who are not familiar with mechanical testing, or who are not aware of the pitfalls involved in the dynamic testing of small amounts of setting materials. The test system displays high versatility, and is capable of performing various static and dynamic tests related to axial tension and compression. The deformation signal feedback loop permits the crosshead to accurately perform sinusoidal deformations on the shrinking specimen on a submicrometer level. The electronics used to process the signals excludes the risk of electronically based phase shifts in stress-strain measurement when submicrometer deformations are applied at frequencies ≤ 1 Hz. The use of a light sensor device proved capable of detecting the initiation and duration of the light irradiation process for cure-on-demand materials. Preliminary experiments on commercially available chemically activated and light-activated resin composites indicate that the universal testing machine is highly useful for detailed static and dynamic studies of the mechanical behavior of dental restorative materials during setting. The sophisticated mechanical experiments provide a sound basis for characterizing the mechanical properties of dental restorative behavior during setting by means of modeling.
**Introduction**

Appropriate modeling of linear viscoelasticity of dental resin composites during setting requires a good understanding of the mechanical properties of the materials involved. Experimental tests are necessary to find out the important characteristics of the composites, and hence provide the data for the modeling investigation of linear viscoelastic behavior of dental composites during setting.

In the next section, several mechanical test methods for measuring the mechanical behavior of materials were screened for use as test method in this research project. The choice of test method is made on requirements that must be met by the method when dealing with shrinking dental resin composites. Various tests were performed on commercially available dental resin composites to characterize the mechanical behavior of setting composites, and to make an inventory of the possibilities and limitations of the chosen, and in this project further improved, dynamical test system. Details of the equipment, experimental procedures and materials are given in the remainder of this chapter. Unless stated otherwise, the mechanical tests referred to in other chapters are performed as described in this chapter.

**Choice mechanical test method**

Different mechanical test methods and testing instruments for measuring the mechanical behavior of materials have been standardized and are described in the publications of the American Society for Testing and Materials [1]. Besides the ASTM standard tests, also general reference books have been published on testing polymers and viscoelastic materials [2-4]. For selecting the test method for measuring the mechanical behavior of dental resin composites during setting, it is necessary to make an inventory of requirements that must be met by the method.

**Requirements mechanical method**

The most important requirement of all is that the method must produce reliable experimental data of dental resin composites. To be genuinely useful, the method must generate data (i) with high acquisition rate to ensure proper characterization of the material properties by means of modeling, (ii) without the influence of the
instruments, electronics, and software as used in the method, (iii) which is representative for the whole material under study rather than on one (weak) part of the material, and (iv) without damaging the internal structure and/or affecting the setting process of the material.

As our investigation is focused on dental resin composites, the test method must be suitable for chemically activated as well as light-activated composites. This means that the method has to deal with material size close to clinical amount in which the structure changes from soft to hard in a short period in time. In the case of light-activated composites, the instrument must be accessible for positioning a dental light source nearby the specimen.

It must be possible to apply deformations in the submicrometer range. In this case, the straining of the material is within the range of linear viscoelasticity (<0.5%). As a result, the mechanical behavior of dental resin composite can be modeled with simple linear viscoelastic models, consisting of springs and dashpots. The choice for applying deformation instead of load was based on the findings that it was difficult to control the applied load on a shrinking composite wherein the structure changes rapidly from soft to hard. Deformation applied as a continuous known function in time (e.g., sine shape) is preferred, because this would greatly reduce the computational effort as the model equations could be solved analytically to yield the stress as a function of the unknown material parameters and strain (appendix A).

It is important that straining and stressing of the setting material is homogeneous and that the distribution of both variables is well defined. Further, to reveal as much as information about the material behavior under shrinkage strain rate conditions, the test method must be feasible with many specially designed test procedures (requires sophisticated software and flexible instrumentation). Our main interest is focused on monitoring the mechanical behavior under shrinkage strain rate conditions. This means that the test method must be able to apply deformations in the low frequency range of 0.001-1.0 Hz.

At last but not at least, some form of temperature control must be used, because changes in temperature does not only affects the setting process, and as a result the viscoelastic properties, but also produce expansion or shrinkage of the materials, resulting in thermal strains and stresses. In addition, some water control is also desired, because dental restorative materials in functioning are exposed to saliva. In the next section, several mechanical test methods will be screened and the choice of test method is made on requirements as stated above.
Mechanical test methods

In general, mechanical test methods for measuring mechanical behavior can be divided into two groups: static and dynamic test methods. In static test methods, the material can be (i) forced a given amount and the change in length of the specimen in time is measured, (ii) deformed a given amount and the change in force of the specimen in time is measured, or (iii) deformed at a constant rate and the buildup of force is measured. Since we are dealing with setting restorative materials in which the structure changes with time, tests under (i) load control or (ii) deformation control reveal the axial shrinkage strain or stress development with time [5-9]. Dynamic test methods measure the response of a material to pulse or oscillatory sinusoidal cycling. The dynamic behavior of setting resin composites is of interest since it provides us additional information, especially in the remainder of the setting process, where the shrinkage strain rate is slow.

![Diagram of experimental methods](image)

**Figure 3.1** Summary of experimental methods in time and frequency domains [3]. The gray area represents the frequency region of interest for this research project.

There are many types of dynamic instruments, each limited for a certain frequency range, but together capable of covering the range from a small fraction of a load cycle per second up to millions of load cycles per
second (Fig. 3.1). The general type of dynamic instruments are nonresonant vibration (torsion pendulum, rheometer, servo(hydraulic) controlled universal testing machine), resonance vibration (pulse induced vibrometer), and wave (ultrasonic) instruments. The instruments measure either shear, tensile, bending, torsion, or biaxial. The instruments are described in detail in literature [1-4].

Our interest is focused on monitoring the mechanical behavior under shrinkage strain rate conditions. Therefore, ultrasonic methods [10-12] and resonant vibration methods [13-16], which are used to determine the material response in the high-frequency range (Fig. 3.1), are not of interest.

The torsion pendulum method performs oscillations in the low (0.1-120 Hz) frequency range [17-20]. However, the disadvantage of this method is that the materials under study must have been set to a sufficient degree of hardness in order to remain the specimen shape. In addition, a large amount of material is necessary, and it is complicated (or even impossible) to measure the torsion deformation on the material.

Two instruments are candidates for monitoring the polymerization reaction of resin composites in the subresonant vibration range, namely the rheometer (shear) and the universal testing machine (compression, tension, and torsion). The oscillating rheometer according to Wilson [21] is the most popular device in dental research for monitoring the rheological properties of chemically activated [22] and light-activated [23] dental restorative materials. The lack of possibility to control the applied oscillatory deformation to the material results in a decrease of the amplitude of the oscillating response when the stiffness of the material increases. As a consequence, the instrument can only monitors the early stage of setting. Since we want to monitor the mechanical behavior throughout the setting process, this oscillating rheometer according to Wilson is not suitable for our research project.

Nowadays commercially rheometers (Rheometric, Triton, Bohlin, HAAKE) and universal testing machines (Zwick, Instron, Hounsfield) have become available to perform controlled stress and strain tests on materials. Traditionally, the rheometer and the universal testing machine are designed especially for large amount of material, respectively liquids, suspensions, pastes ([24-26]) and solids ([27]), for which the structure do not or slowly (physical ageing) change with time [28]. Both instruments are capable of performing a wide range of static and dynamic tests.
Two aspects of the universal testing machine were decisive for the choice for using this testing method in this research project. First, the universal testing machine can measure the shrinkage load development of setting composite in the longitudinal direction, while this material behavior cannot be determined by a rheometer (transverse direction). Second, the study of Feilzer and co-workers showed that with proper adjustments on a commercial universal testing machine it was possible to measure the mechanical behavior of setting dental restorative on a submicrometer level [7].

For generating reliable data, certain aspects of a commercial testing machine have been improved. With the knowledge gained in this modification process a second automated testing machine was developed and produced at the Department of Dental Materials of ACTA. Both testing machines were capable of performing various tests on dental restorative materials during setting.

Several tests were carried out on a control (steel) specimen, and commercially available dental restorative composites for the purpose to evaluate the limitations of the testing machine in generating stress-strain data on dental restorative materials during setting. Since both testing machines were capable of generating data on the same level of accuracy, the limitations found for the modified commercial testing machine is also valid for the home-build testing machine.

**Test equipment and facilities**

**Universal testing machines**

The experiments were conducted on two automated servo-controlled testing machines: a commercial Hounsfield (Fig. 3.2) and a home-build ACTAIntense (Fig. 3.3). To enable the recording of periodically applied deformation cycles on a micrometer level, the gearbox of the commercial testing machine was modified to eliminate the play when the motion direction of the cross head was reversed. At the same time, the maximum cross head speed was reduced to 40 mm/min. The maximum cross head speed of the ACTAIntense was 200 mm/min. The minimum cross head speed cannot be strictly specified, as it is regulated by the settings in the application software. Both machines were equipped with a load cell of 1000 N and connected, via a data-acquisition console, to a desktop computer. The load cell was regularly checked with standard weights and calibrated if applicable.
Experimental considerations

Figure 3.2 Test system: (a) modified universal testing machine (H10KM, Hounsfield), (b) data-acquisition console (20-90, Intrumat), (c) extensometer (Millitron 1202D, Mahr), (d) Pentium Pro computer (Intel/200 MHz), and (e) specimen mounting device with two LVDT transducers (1300, ±2.0 mm, Mahr).

Application software for Windows® 95/98 was developed for controlling and monitoring the experiment and collecting the data (time, load, deformation, temperature, and light irradiation signal). Throughout this investigation, the chemically activated resin composites were measured solely on the modified Hounsfield machine and the light-activated composite solely on the ACTAIntense. This strict distinction was a consequence of the course of time within this research project, were the study on light-activated composites coincided with the production of the ACTAIntense testing system.

Specimen mounting device

In the experiments, two specimen mounting devices were used: one for chemically activated materials (Fig. 3.2), and one for light-activated materials (Fig. 3.3). The device for the chemically activated materials was based on the same principle as described by Alster et al. [29]. The upper steel disk was connected to the cross head and the lower steel disk to the stationary part of the framework.
In the mounting device for light-activated materials, the lower steel disk was replaced by a glass plate, thereby creating a light activation method which simulates the clinical situation as close as possible. The glass plate was mounted on a steel tube, which was screwed in the metal basement attached to the stationary part of the framework. The metal basement provides enough space for various types of dental light sources.

By using these special designed mounting devices two requirements were met for performing reliable measurements on small amount of
materials. First, the applied submicron deformation was measured directly at the level of the specimen by two LVDT\(^1\) transducers. In this situation, the compliance of the testing machine (bars, joints, load cell), which can introduce errors in the situation were the deformation of the specimen is measured by the displacement of the motor, was circumvented.

![Diagram of experimental setup](image)

**Figure 3.4** Dental restorative material bonded in specimen mounting device.

Second, the axial deformation was applied on cylindrical shaped specimen, thereby generating uniform tension or compression load in the specimen. With the bonding procedure, the normal load in the cylindrical specimen is distributed uniformly over the ends of the specimen and as a result, the load pattern at the end will be the same as everywhere in the specimen (Fig. 3.4). Deformation in the bonding layers, which was spread out in a thin layer, was assumed to be neglectable small.

The signals of the two transducers were averaged, thereby reducing the noise in the deformation data and cancelling tilting effects. This averaged signal was fed back into a control loop, embedded in the application software, for fine-tuning the motor-driven cross head movement on the specimen (Fig. 3.5). To avoid the risk of bending under compression, the length/diameter ratio of the cylindrical

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\(^1\)Linear Variable Differential Transformers [3]
specimen was chosen to be within the range of 0.15-1.0 [30]. Unfortunately, it was not possible to implement a device in the specimen mounting device for monitoring the lateral deformation (perpendicular to the direction of the applied deformation) of the specimen. As a result, no Poisson’s ratio $v(t)$ could be determined.

![Diagram of experimental setup](image)

**Figure 3.5** Feedback loop for fine-tuning the cross head movement on setting restorative material.

**Specimen preparation and bonding procedure**

Chemically activated resin composites

The freshly mixed resin composite (1:1 w/w) was inserted into a cylindrical, lightly greased, and deformable paper matrix that was placed around two parallel opposing steel disks (Fig. 3.4). To ensure optimal bonding between the resin composite and the disks, the bonding surface of the steel disks was wet ground smoothly with sandpaper grit 600, sandblasted with aluminum oxide (Korox, 50 μm, Bego) for approximately 2 minutes under 5 bar air pressure, rinsed with acetone,

$v(t) = \frac{-\text{lateral strain}(t)}{\text{axial strain}(t)}$ [30]
Chapter 3 | Experimental considerations

dried, and silanized with the Silicoater technique (Kulzer), introduced by Tiller and Musil [31-32]. The technique consists of fusing a thin, silicate layer (SiOx-C) on the surface of the alloy [33]. After that, a silane coupling agent is spread on the silicate layer, which provides the chemical bonding to dimethacrylates composites. Contrary to the manufacturer's recommendations, neither the Silicoater Opaque nor any other bonding resin was used to protect the silanized surface from hydration. To avoid impairment of the adhesion, the resin composite was placed between the opposing steel disks within 30 minutes [31].

The disks had a diameter (d) of 5.4 mm and were separated by a distance (h) of 5.0 mm, creating a bulk restoration with a C-factor of 0.5 (=d/2h). Prior to the start of the experiment the upper steel disk was moved down until it reached the pre-adjusted height of the specimen. The start of the experiments always took place within the working time of the chemically activated materials.

Light-activated resin composites

The light-activated resin composite was inserted into a cylindrical, lightly greased, Teflon mold that was placed on the glass plate (Fig. 3.4). To ensure optimal bonding between the composite and the glass plate (float glass, Bakker), the glass surface was gently sandblasted with aluminum oxide (Korox, 50 μm, Bego) for approximately 20 seconds under 4 bar air pressure, rinsed with acetone, dried, primed (Rely X ceramic primer, 3M), and finally coated with a pressurized air spread adhesive layer (Scotchbond Multi-purpose, 3M), which was light-cured for 40 seconds (Elipar Highlight, standard mode, ESPE). The bonding surface (d=3.1 mm) of the steel disk was prepared as described in the previous section. The Teflon mold had a diameter (d) of 3.1 mm and height (h) of 1.6 mm, creating a layer restoration with a C-factor of 1.0 (=d/2h). The composite layer thickness was thin enough to ensure proper light activation [34], and thick enough to exclude the effect of compliance of the specimen mounting device [35].

Materials

The materials used in this investigation were two commercially available chemically activated resin composites (Clearfil F2, batch CU-0235 & CC-0135, Kuraray and Silar, batch: A-4KE1 & B-4KH1, 3M) and two commercially available light-activated resin composites (Z100 MP A3, LOT: 19981009, 3M and Silux Plus, LOT: 19981015, 3M). A steel
specimen (Fig. 3.6) served as a control. The chemically activated composites were handled and mixed (1:1 w/w) according to the manufacturer's instructions, while the light-activated composites were polymerized for 40 seconds with a light curing unit (Elipar Highlight, standard mode, ESPE) at a distance of 4 mm. The intensity at the light exit tip (\(\varnothing=8.95\) cm) was 600 mW/cm\(^2\) (hand-held radiometer, model 100, Demetron).

![Steel specimen](image)

**Figure 3.6** Steel specimen.

**Testing and measurement**

Different static and dynamic tests were performed to evaluate the limitations of the testing systems, and to check if the system satisfies the requirements that must be met for generating data of the mechanical behavior of dental restorative materials during setting. The choice for applying deformation cycles instead of load cycles was based on the findings that it was difficult to control the load cycles on a material wherein the stiffness changes rapidly from soft to hard. The applied deformations were kept small (1.0-2.0 \(\mu\)m) in order to generate stresses that can be studied with linear viscoelastic models [36].

**Static test: axial shrinkage stress development**

In this static test, axial shrinkage of the specimen was prevented by the cross head in keeping the original height of the specimen constant. This process was controlled by the displacement signal of the LVDT transducers, which drove the cross head back to the original specimen
height as soon as axial shrinkage was registrated. Under this constraint condition, the increase in material stiffness will lead to the development of shrinkage forces in the specimen, which was monitored by the load cell. The normal stress ($\sigma$) was calculated using the following equation:

$$\sigma = \frac{F}{A}$$

in which $A$ is the cross-sectional area of the cylindrical specimen ($m^2$), and $F$ the recorded load response of the specimen ($N$).

Since stress data plays a crucial role in the choice of the model and calculation of its material parameters (Fig. 4.3), the reproducibility of the stress data must be analyzed. Therefore, repeated experiments on one chemically activated composite and one light-activated composite were performed at constant specimen height; i.e., keeping the deformation signal at $0\pm0.01 \, \mu m$.

After insertion of the freshly mixed Silar (1:1 w/w) into a cylindrical paper ($d=3.1 \, mm$), the disk-to-disk distance ($h$) was set at a pre-adjusted value of $1.60\pm0.05 \, mm$ ($C=1.0$), and the experiment on the Hounsfield machine was started. For the same purpose, Silux Plus was inserted into a Teflon mold ($d=3.1 \, mm$), the disk-to-glass distance ($h$) was set at a pre-adjusted value of $1.60\pm0.05 \, mm$ ($C=1.0$), and the experiment on the ACTAIntense was started 5 s prior the light irradiation process. The light irradiation process with duration of 40 s was measured with a home-build light sensor device at the level of the specimen. With the cross head speed set at $0.025 \, mm/min$, and the extensometer set at the lowest deformation range of $20 \, \mu m$, the original specimen height could be kept constant within $\pm0.01 \, \mu m$. The data were collected simultaneously by the computer (software version 3.14) at a rate of 18 points per second.

![Figure 3.7](image)

**Figure 3.7** Repeated shrinkage stress curves ($n=3$) for Silar ($C=1$) and Silux Plus ($C=1$). For clarity, the results of the light-activated composite are shown at two different time-scales.
The experiments (n=3) were performed at room temperature (23±1 °C).

The position of the light sensor appeared adequate for detecting accurately the start and duration of the light irradiation process. Hereby, the experimenter could assign stress-strain data correctly to the setting time of light-activated composites.

A requirement for measuring load with a mechanical transducer is that the internal structure of the restorative material has achieved enough strength to overcome the elastic resistance of the load cell. Under the experimental conditions (temperature, specimen geometry, load cell capacity) the chemically activated Silar stays 4 minutes in the pre-gel phase, in which the viscous flow behavior predominates over the elastic behavior, while the analogous light-activated Silux Plus (Fig. 3.7) stays only 2 seconds in this favorable stress-free stage of setting. The longer pre-gel phase of Silar is a result of the slower polymerization reaction rate of the material [36]. The slow shrinkage stress development of Silar is clinically favorable, because the integrity of the composite-tooth interface is slowly challenged during the early phase of polymerization, when the bond between the tooth tissue and the composite is still maturing. Since the attained stress values were lower or just reached into the range of reported tensile bond strengths of dentin bonding agents [37], the early maturing dentin-bond composite interface will survive the shrinkage stresses, which enhanced the chance on a tight sealed restoration.

Several operation stages in the experiment method (specimen preparation, temperature, data-acquisition) are subjects to errors, which together determine data reproducibility. The large difference between the reproducibility of the Silar stress curves (standard error 5-7 %) and Silux Plus stress curves (standard error <3 %) can mainly be attributed to the specimen preparation. Specimens of Silux Plus were more constant in homogeneity and composition, because they were prepared directly from a batch as received from the manufacturer. Specimens of chemically activated composites were prepared by hand-mixing two pastes (1:1 w/w) within 40 seconds. With this preparation method it is difficult, and probably impossible, to achieve specimens with a constant level of homogeneity and composition.

At the start of the experiment, both type of specimens were free of internal stresses, because the composites were inserted with the aid of a wide-diameter syringe tip. In the further course of this investigation, all types of composites were measured three times, because the standard error was below 10 %, which was set as maximum tolerance. Data from
an experiment coinciding best with the average response were used for further analysis and modeling.

**Static test: axial shrinkage strain development**

In this static test, the cross head movement towards the shrinking specimen prevented axial shrinkage stress development in the specimen. This process was controlled by the load cell signal, which drove the cross head towards the specimen as soon as a load signal was monitored. Under this condition, the axial displacement was monitored by the LVDT transducers and should be related to the axial shrinkage of the specimen in the mounting device. The axial strain ($\varepsilon_{\text{axial}}$) is defined as:

$$\varepsilon_{\text{axial}} = \frac{\Delta L}{L_0} \quad (3.2)$$

where $\Delta L$ is the displacement recorded by the LVDT transducers and $L_0$ the height of the specimen before setting.

The axial shrinkage strain of dental composites, bonded to the two opposing rigid surfaces could also be derived indirectly by the free volumetric shrinkage strain, as measured with mercury dilatometry, with the following relation found by Feilzer et al. [38]:

**Table 3.1** Relation between axial shrinkage strain ($\varepsilon_{\text{axial}}$) and volumetric shrinkage strain ($\varepsilon_{\text{vol}}$) for dental resin composites bonded at different configuration (C-factor) geometry [38].

<table>
<thead>
<tr>
<th>C-factor</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{\text{axial}}$</td>
<td>0.36$\varepsilon_{\text{vol}}$</td>
<td>0.45$\varepsilon_{\text{vol}}$</td>
<td>0.60$\varepsilon_{\text{vol}}$</td>
<td>0.65$\varepsilon_{\text{vol}}$</td>
<td>0.75$\varepsilon_{\text{vol}}$</td>
<td>0.85$\varepsilon_{\text{vol}}$</td>
</tr>
</tbody>
</table>

The axial shrinkage strain of the specimen in the mounting device is of interest, because in dynamic tests, wherein the cross head cycles up and down around the original specimen height, the strain caused by axial shrinkage must be taken into account when the stress data (Fig. 5.2) is used in the modeling procedure (Fig. 4.3). In this study, the cross head displacement due to axial shrinkage of a chemically activated composites was measured on the modified Hounsfield testing machine, and the results were evaluated with the results obtained with mercury dilatometry.
A series of zero load tests at different cross head speeds were performed with Clearfil F2 to determine the axial shrinkage deformation of this chemically activated resin composite bonded between two opposing steel disks. After insertion of freshly mixed Clearfil F2 into the paper matrix (d=5.4 mm), the disk-to-disk distance (h) was set at a pre-adjusted value of 5.0 mm (C=0.5) and the experiment on the testing machine was started. During the experiment, the cross head continuously followed, at five different speeds (8, 16, 40, 80, and 400 μm/min), the axial displacement of the specimen, i.e., kept the load signal at zero. The data were collected simultaneously by the computer (software version 2.80) at a rate of 2 points per second. All experiments (n=1) were performed at room temperature (23±1 °C). The extensometer was set at the deformation range of 200 μm. One hour after the start of the experiment, the restorative material was subjected to tensile loading with a cross head speed of 160 μm/min until fracture.

Volumetric shrinkage strain measurements on Clearfil F2 (n=3) were performed with a mercury dilatometer at 23±0.1 °C, using the procedure described by De Gee et al. [39]. The bonded axial shrinkage strain (ε_axial) for the C-factor 0.5 was derived from the volumetric shrinkage strain (ε_vol) by the conversion factor given in Table 3.1.

![Graphs showing cross head displacement and axial load](image)

**Figure 3.8** (a) Cross head displacement towards Clearfil F2 and (b) axial load on Clearfil F2 (n=1) at different cross head speeds (note different x scale). Mean axial displacement derived from dilatometry data (n=3) is also incorporated (—)

The test system was able to keep the cross head motionless when the load signal was within 0±0.05N. A disadvantage of this low threshold value in the load signal was that noise in the load signal triggered the computer to activate the cross head movement. As a result, a small load signal was induced due to the movement of the load cell weight. At this stage of setting, the specimen (C-factor=0.5) was too fluid to balance this small load and, as a consequence, the cross head moves either away.
or towards the specimen at the pre-adjusted cross speed (Fig. 3.9). It was up to the gel point of Clearfil F2, approximately 3 minutes after mixing, that the composite achieved the required stiffness to overcome the elastic resistance of the load cell. From this point in time on, the software was able to regulate the cross head movement correctly on basis of the forces acting on the load cell.

![Graph](image)

**Figure 3.9** Derivatives of axial displacement towards Clearfil F2 at different cross head speeds (n=1). Derivative of mean axial displacement derived from dilatometry data (n=3) is also incorporated (−).

In cases where the cross head speed was set too low (8-16 μm/min), the cross head was not able to follow the rapid composite shrinkage; i.e., to zero the shrinkage force. Figure 3.8 shows that the large influence of the cross head speed on the recorded axial displacement made this test system not suitable for axial shrinkage strain determinations for dental restorative materials with low C-factor. Implementing a second feedback loop for the load signal in the application software would make the test system far better for axial shrinkage strain measurements, because the cross head movement could then be controlled accurately. The current feedback loop on the deformation signal (Fig. 3.5) was insufficient for accurate load control on the specimen, because the feedback loop software was not geared to the rapid stiffness change of the material during setting.

In mercury dilatometry, the flow ability of materials has less influence on the shrinkage strain results, because the driving force behind the
transducer displacement is not regulated by an external device, but by the specimen itself. An attendant advantage of this free shrinkage measurement method is that the displacement transducer was activated by a few milli Newtons, and therefore offers to measure the total (pre- and post-gel) shrinkage strain. A disadvantage of dilatometry is that higher amounts of composite (200-300 mg) are required than in the test system (100-200 mg). As a result, the polymerization reaction will proceed slightly faster due to higher temperature of the specimen as more heat will be released from the exothermic setting specimen.

The study of Feilzer and co-workers showed that composites exhibit a different shrinkage behavior under bonded condition [38]. Composite shrinkage under free (dilatometry) condition is equally distributed in three dimensions, whereas under bonded (dynamic test) condition it becomes more directed towards the bonding sites. An increase of the C-factor (i.e., when the composite layer is decreased), the volumetric shrinkage is gradually converted into the axial direction. The conversion factors in Table 3.1 provide us to calculate a reliable estimate of the shrinkage behavior under bonded condition from dilatometry results. In the course of this research project, the axial shrinkage strain data of dental resin composites was determined indirectly with mercury dilatometry by the conversion factors provided by Feilzer et al. (Table 3.1).

**Dynamic test: pulse sinusoidal strain cycles**

The dynamic behavior of resin composites during setting is of interest, because it provide us additional information, especially in the remainder of the setting process, were the polymerization rate is low. In this study, a pulse cycle experiment was performed on a chemically activated resin composite during setting. Freshly mixed Clearfil F2 was inserted into the paper matrix (d=5.4 mm), and after setting the disk-to-disk distance (h) at a pre-adjusted value of 5.0 mm (C=0.5), the experiment on the Hounsfield machine was started.

The experiment consisted of periodically cycling the cross head sinusoidal around the specimen height with a maximum displacement of 2 μm (0.04 % strain). In the periods between the cycles (hold periods), the cross head continuously followed the axial shrinkage of the specimen, i.e., kept the load signal at zero. The motor-controlled cross head speeds in the hold and cycle periods were 20 and 40 μm/min respectively. During the experiment, the data were collected simultaneously by the computer (software version 3.11) at a data rate of 18 points per second. The extensometer was set at the range of 200 μm.
A control experiment was performed with a steel specimen (d=2.5 mm, h=30 mm), which was clamped directly between the cross head and base of the testing machine (Fig. 3.6). The maximum axial deformation applied in compression and tension was 1 μm (=0.0033 % strain). This had to be smaller than the deformation of the composites, due to the high Young’s modulus of steel. The deformations were applied around a tension load of 50 Newton to exclude the risk of bending of the steel specimen during compression. Except for the control (n=1), all experiments were repeated three times and were performed at room temperature (23±1 °C). One hour after the start of the experiment, the restorative material was subjected to tensile loading with a cross head speed of 160 μm/min until fracture.

The strain produced from periodically cycling was isolated from the displacement using:

\[ \varepsilon = \frac{\Delta h_{\text{cycle}} - \Delta h_{\text{start}}}{h_0 - \Delta h_{\text{start}}} \]  

(3.3)

in which \( h_0 \) is the initial specimen height (m), \( \Delta h_{\text{cycle}} \) the cross head displacement during a cycle (m), and \( \Delta h_{\text{start}} \) the cross head displacement at the start of a cycle (m). The normal stress on the specimen was calculated by Equation (3.1).

The sign convention for data generated by dynamic tests is stated in the following manner. For the cross head movement away from the specimen the load and deformation signal are positive. For the cross head movement towards the specimen the load and deformation signal are negative. By way of exception, the cross head movement towards the specimen due to shrinkage; i.e., keeping zero load on specimen, the deformation signal is stated positive.

An important prerequisite for the performance of deformation cycles in the submicrometer range is the elimination of the play in the machine,

<table>
<thead>
<tr>
<th>Material property</th>
<th>With cycling (^a) (n=5)</th>
<th>Without cycling (^b) (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>10.0 (0.5)</td>
<td>10.0 (0.6)</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>34.7 (2.6)</td>
<td>36.8 (3.1)</td>
</tr>
</tbody>
</table>

\(^a\) Section: Dynamic test: pulse sinusoidal cycles  
\(^b\) Section: Static test: axial shrinkage strain development
since it reverses from compression to tension or vice versa. The modifications carried out on the Hounsfield machine used in this study appeared adequate on the basis of the results with the control specimen. These showed a near-perfect sine pattern for the cross head displacement during a complete deformation cycle, indicating that the play in the machine had been eliminated.

Another important requirement is that the deformations applied on the restorative materials do not negatively influence the structural integrity during setting. A strain of $\leq 0.04\%$, as chosen in this study, satisfied this requirement [40]. The Student’s t-test with pooled variance ($p<0.05$) demonstrated that the tensile strength of the resin composite, which was subjected to deformation cycles during setting, was similar to experiments where no cycles were used (Table 3.2). This gives the experimenter the opportunity to perform additional tests on the polymerized specimen in the testing machine.

A survey of the data recorded during the initial 10 minutes of the setting process is given in Figure 3.10a for the resin composite. The figure illustrates the applied deformation cycles superimposed on the shrinkage curve (left y-axis), and the resulting load response (right y-axis) of the material. Although the cross head displacement towards the composite results from axial shrinkage, it was not the same as the actual axial shrinkage of the composite.

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**Figure 3.10** Data collected in pulse sinusoidal deformation experiment with Clearfil F2. For clarity, only data for the first 25 minutes of the setting process is shown.
As stated in the previous section, part of the shrinkage may not be registered correctly at the very start of the experiment, when the composite is still too fluid to "regulate" the cross head, and the recorded displacement depend heavily on the pre-adjusted cross head speed (Fig. 3.8a).

The shape of the stress-strain curve obtained at several sinusoidal pulses resembles a hysteresis loop for the resin composite, and a straight line for the control specimen (Fig. 3.11). The straight line of the stress-strain curve for steel is due to pure elastic behavior. Hysteresis loops result when the load response is time-dependent. This still seems to be the case for Clearfil F2 at a 14-minute setting, the point at which curve 4) was recorded. The hysteresis area in the stress-strain curve is a measure of energy loss from the composite during cyclic deformation. This energy dissipation is probably due to the viscoelastic behavior of the composite rather than to any response time of the motor-driven testing machine or the electronic parts in the data-acquisition console. Dynamic tests in our laboratory revealed that RC-filters in the electronics of the test system started to influence the stress-strain data when sinusoidal cycles with amplitude of 1.0 \( \mu m \) and frequencies higher than 1.0 Hz were applied to the steel specimen.

![Stress-strain curve](image)

**Figure 3.11** Stress-strain curves for Clearfil F2 under sinusoidal pulses at 1) 306, 2) 448, 3) 658, and 4) 872 seconds setting (Fig. 3.10). The stress-strain curve for the steel specimen is also incorporated.
The slope of the line from the origin to the point of maximum strain in the curve is a measure of the elastic component (Young's modulus) of the viscoelastic composite. As expected, the stiffness of the setting composite increases with time. Generally, it is often found that values measured in compression are somewhat higher than those measured in tension due to the presence of filler and imperfections (flaws and microcracks) in the specimen [4]. The Student's t-test with pooled variance (p<0.05) demonstrated that the values of Young's modulus calculated in the tension phase of the stress-strain curve were similar to the Young's modulus values calculated in the compression phases (Fig. 3.12). Obviously, the amplitude of the applied deformation was small enough to exclude the risk of higher Young's modulus values in compression phase.

The accuracy of the test system was tested with a steel specimen. The slope of the stress-strain curve of steel calculated in this study (194±4 GPa) is in agreement with the value 200±10 GPa given in reference books [30].

A drawback of this pulse method, wherein between cycling the axial shrinkage displacement of the specimen is followed by the cross head, is that the shrinkage strain curve is incorporated in each individual deformation cycle. Although Equation (3.3) largely diminish the

![Figure 3.12 Young's modulus development of Clearfil F2 calculated from the tension and compression phase in the isolated stress-strain cycles (Fig. 3.11).](image)
shrinkage contribution in the isolated strain cycle, the second part of the cycle still contains a shrinkage contribution, because shrinkage does not stop at the beginning of the cycle ($\Delta h_{\text{start}}$), but still proceeds. Especially in the early stage of setting, where the shrinkage development proceeds rapidly, the isolated strain cycle deviates dramatically from a symmetrical sinusoidal function. For modeling stress-strain data, the latter form of deformation is preferred, because this would greatly reduce the computational effort and accuracy of the modeling procedure as the model's equation could then be solved analytically (appendix A). Next section shows that analytically shaped sinusoidal cycles throughout the setting process can be obtained by performing oscillatory sinusoidal cycles around a constant specimen height.

Dynamic test: oscillatory sinusoidal strain cycles

For modeling the mechanical behavior of resin composites during setting, the material parameters associated with the model were assumed to be constant with time. Since setting of composites is a dynamic process, wherein its structure changes from soft to hard, this assumption holds only when the time span of the isolated stress intervals applied to the modeling procedure (Fig. 4.3) was kept small with respect to the rate of polymerization reaction. Present-day light-activated dimethacrylate composites change rapidly from soft to hard in the setting process. Therefore, for generating stress-strain data on light-activated composites, the deformation cycles must be kept small; i.e., time intervals of 1 s or less. Smaller deformation cycles require higher acquisition rates for the stress-strain data in order to obtain enough data points for the modeling procedure (Fig. 4.3). In this study, an oscillatory test method was performed on Z100 to evaluate if the test system was able to generate analytically shaped sinusoidal cycles on fast setting composites.

After insertion of the light-activated composite into the Teflon mold ($d=3.1$ mm), the cross head was lowered until the extensometer displayed the pre-adjusted distance between the upper steel disk and lower glass plate ($h$) of 1.60 mm, creating a specimen geometry with C-factor=1.0. The test method was programmed to perform two frequencies with amplitude of $1.00\pm0.01$ $\mu$m (0.0625 % strain). First, a frequency of 1.0 Hz was applied for 50 seconds on the fast setting composite, followed by a frequency of 0.1 Hz for the time period of one hour. After the period of oscillatory cycling, the cross head moved towards the composite in a prescribed time period of 200 seconds to relieve the shrinkage load, followed by a period wherein the load signal was maintained zero for
100 seconds. Finally, the composite was subjected to tensile loading (120 µm/min) until fracture.

The light irradiation process (Elipar Highlight, standard mode, ESPE) was measured with a light sensor device at the level of the specimen. The distance between the light exit tip (Ø=8.95 cm) was equal to the thickness of the glass plate (4 mm). During the measurement, the data were collected simultaneously by the computer (software version 3.14), via a data acquisition console, at a rate of 100 points (1.0 Hz period) and 18 points (0.1 Hz period) per second respectively. The experiments were started 5 seconds prior to the light irradiation process and were repeated three times at room temperature (23±1 °C) on the ACTAIntense. The oscillatory deformation was measured with the extensometer (CAH Card, Dimed) in the range of 20 µm.

Figure 3.13 (a) Strain and (b) stress data of Z100 (C-factor=1.0) collected with a dynamic oscillatory test. The signal of the light sensor, which measured the initiation and duration of the light activation process, is given in arbitrary units. The (c) shrinkage stress and (d) dynamic stress response were isolated from (b) experimental stress data via FFT smoothing and substraction (b-c) respectively.
Despite the rapid increase of the composite's stiffness, the test system was able to generate analytically shaped sinusoidal deformation cycles (Fig. 3.13a). In the light irradiation period, the amplitude of the strain was fractional higher than the preset value (0.0625 %), because the feedback system compensated the cross head movement on the fast setting specimen too much. The higher strain amplitude did not, however, lead to errors in the modeling results, because not the preset, but the measured sinusoidal strain function was utilized in the modeling procedure.

Light irradiation of Z100 was initiated after at least four oscillatory strain cycles were applied on Z100, because laboratory tests on a control specimen revealed that an experimentally applied sinusoid, which has a starting point, converges within four cycles to a mathematical sinusoid, which has no beginning or end (see next section).

The advantage of performing oscillatory sinusoidal deformations around a constant specimen height is that the oscillatory stress response is superimposed on the shrinkage stress curve. These stresses of different origin can be isolated from each other with the Fast Fourier Transform (FFT) smoothing procedure in Origin (version 5.0, Microcal). Analysis of the oscillatory stress-strain (Fig 3.13a+d) directly, resulting in the storage modulus ($E'$) and the loss modulus ($E''$), provides valuable additional information for the research on the viscoelastic behavior of dental restorative materials during setting [41].

**Experimental data**

**Sinusoidal deformation data**

Applying a sinusoidal shaped deformation on setting composites will enhance the accuracy of modeling the mechanical behavior of composites, because the differential equations for the different models can then be solved analytically (appendix A). In this study, an oscillatory deformation was applied to a control specimen to investigate the sine development with time.

A steel specimen ($d=2.5$ mm, $h=3.5$ cm) was clamped between the cross head and base of the ACTAIntense (Fig. 3.6). The sinusoidal deformation (frequency $1.0$ Hz, amplitude $1.0$ µm) was applied around a tensile load of $50$ Newton to avoid bending of the specimen in the compression phase of the sine. During the experiment, the data were collected simultaneously by the computer (software version 3.14), via a data
acquisition console, at a rate of 100 points per second. The oscillatory deformation was measured with the extensometer (CAH Card, Dimed) in the range of 20 μm.

![Figure 3.14](image)

**Figure 3.14** (a) (--) Experimental applied deformation compared with (—) mathematical sinusoidal deformation. (b) Absolute discrepancy ([experimental - mathematical] * 100 %) between the two oscillatory deformations.

A mathematical sine function has no beginning or end. In practice, however, an experimentally applied sinusoid must have a starting point. As can be seen in Figure 3.14, at least two sine cycles were needed before the cross head was able to reach this mathematically level of oscillations. From this point on, the correlation between the experimental and mathematical sinusoid is good. In future oscillatory tests, the applied sinusoids were considered mathematically after four cycles (discrepancy ≤ 1.5 %).

![Figure 3.15](image)

**Figure 3.15** (a) (--) Cubic spline fit on (—) experimental load data. (□) Specific load values in the curve are chosen with spline interpolation. (b) The noise in the recorded load signal and cubic spline fit was calculated by subtraction of the mathematical sinusoid from load response and cubic spline fit respectively.
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Cubic spline interpolation on load data

To estimate the model parameters, the model’s response was matched as close as possible to experimental stress by the use of a least-square method (Fig. 4.3). The disadvantage of the least-square method is that in presence of measurement noise, the model parameter estimates will be biased [42]. Figure 3.15b shows that noise in the load response is white noise [43]. One possibility to reduce the bias is to employ cubic splines interpolation.

Cubic spline interpolation is a useful numerical tool to reduce the noise in the load data by constructing a smooth curve through the measured load points (Fig. 3.15a). The noise in the cubic spline fit is substantial lower (Fig. 3.15b), which enhanced the reliability of the model parameter estimates in the modeling procedure. An additional advantage of using cubic splines is that the individual data points in the curve can be selected independently from the original dataset. The best cubic spline interpolation results were obtained when the time span between the selected points in the fit was longer than the sampled data points in the original dataset. All cubic spline interpolation operations were performed on a desktop computer, using Matlab (version 5.3, MathWorks).

Conclusions and recommendations

There was a clear need for a mechanical test method which generates reliable quantitative data on the mechanical behavior of dental restorative materials during setting. The test system developed as part of this research project meets these requirements. The test system is capable of performing various static and dynamic experiments which provide a sound basis for research aimed at gaining a better understanding of the mechanical behavior of dental restorative material during the setting process. The test system was not capable of producing a reliable measurement of axial shrinkage-strain data. This property was determined indirectly by mercury dilatometry. In future research, reliable axial shrinkage strain data can be obtained by using the load signal in a feedback loop for the crosshead movement. In addition, the implementation of an optical device in the specimen mounting device would make it possible to measure the lateral shrinkage strain of the specimen during setting, and to calculate the Poisson’s ratio of the material. Alternatively, the Poisson’s ratio could be determined by performing additional shear loading tests on setting materials. To obtain reliable shear stress-strain data on shrinking restorative materials, the rotational test device should meet the requirements set for dynamic testing in a tension-compression direction.
References

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36. See chapter 4 of this thesis.